



AFRL-RZ-WP-TP-2009-2101

BREAKDOWN VOLTAGE OF THERMOPLASTICS WITH CLAY NANOMETER-SIZED FILLERS (POSTPRINT)

**Stephen S. Brandstetter, Lawrence F. Drummy, John C. Horwath, Daniel L. Schweickart,
and Richard A. Vaia**

**Electrical Technology & Plasma Physics Branch
Power Division**

DECEMBER 2008

Approved for public release; distribution unlimited.

See additional restrictions described on inside pages

STINFO COPY

© 2008 IEEE

**AIR FORCE RESEARCH LABORATORY
PROPULSION DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7251
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE**

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YY) December 2008		2. REPORT TYPE Conference Proceedings Postprint		3. DATES COVERED (From - To) 01 June 2003 – 01 March 2008	
4. TITLE AND SUBTITLE BREAKDOWN VOLTAGE OF THERMOPLASTICS WITH CLAY NANOMETER-SIZED FILLERS (POSTPRINT)				5a. CONTRACT NUMBER In-house	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 62203F	
6. AUTHOR(S) Stephen S. Brandstetter and Lawrence F. Drummy (UES, Inc.) John C. Horwath, Daniel L. Schweickart, and Richard A. Vaia (AFRL/RZPE)				5d. PROJECT NUMBER 3145	
				5e. TASK NUMBER 32	
				5f. WORK UNIT NUMBER 314532Z7	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UES, Inc. 4401 Dayton-Xenia Road Dayton, OH				Electrical Technology & Plasma Physics Branch (AFRL/RZPE) Power Division Air Force Research Laboratory, Propulsion Directorate Wright-Patterson Air Force Base, OH 45433-7251 Air Force Materiel Command, United States Air Force	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Propulsion Directorate Wright-Patterson Air Force Base, OH 45433-7251 Air Force Materiel Command United States Air Force				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RZ-WP-TP-2009-2101	
				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RZPE	
11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-RZ-WP-TP-2009-2101					
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Conference paper published in Proceedings of the 2008 IEEE International Power Modulators and High Voltage Conference, publication date: 27-31 May 2008. PAO Case Number: AFRL/PA 08-5006; Clearance Date: 05 Aug 2008. © 2008 IEEE. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.					
14. ABSTRACT The addition of fillers are used commonly in industry to improve physical properties of polymers, such as stiffness, hardness, wear, heat distortion temperature or electrical conductivity, or to reduce the overall raw material cost of a part. The addition of nanometer-sized fillers, or nanofillers, has shown potential for improving the polymer's dielectric breakdown voltage in conjunction with augmentation of its mechanical properties. Five different sets of thermoplastics were tested between opposed cylindrical rod electrodes of 6.4 mm diameter with rounded edges of 0.8 mm radius. All polymers in this study showed an increase in the average dielectric strength from 5 to 56 percent with the nanoscale dispersion of 1.5 wt% organically modified montmorillonite (nanoclay). Most of these increases exhibited statistically significant margins. The tested thermoplastic polymers include nylon-6, low-density polyethylene/ethylene-vinyl acetate copolymer, and polyester.					
15. SUBJECT TERMS breakdown voltage, thermoplastics					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 10	19a. NAME OF RESPONSIBLE PERSON (Monitor) Daniel L. Schweickart 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

Breakdown Voltage of Thermoplastics with Clay Nanometer-Sized Fillers

Stephen S. Brandstetter, Lawrence F. Drummy

UES Inc., Dayton, Ohio

John C. Horwath, Daniel L. Schweickart, Richard A. Vaia

Air Force Research Laboratory, WPAFB, Ohio

Abstract—The addition of fillers, such as talc, mica and carbon black, are used commonly in industry to improve physical properties of polymers, such as stiffness, hardness, wear, heat distortion temperature or electrical conductivity, or to reduce the overall raw material cost of a part. Notwithstanding these opportunities, the addition of micron-sized fillers to a polymer may have detrimental effects on its dielectric characteristics, such as dielectric loss, breakdown strength and dielectric durability. Recently, the addition of nanometer-sized fillers, or nanofillers, has shown potential for improving the polymer's dielectric breakdown voltage in conjunction with augmentation of its mechanical properties. Five different sets of thermoplastics were tested between opposed cylindrical rod electrodes of 6.4 mm diameter with rounded edges of 0.8 mm radius. The applied voltages were at 60 Hz. All polymers in this study showed an increase in the average dielectric strength from five to fifty-six percent with the nanoscale dispersion of 1-5 wt% organically modified montmorillonite (nanoclay). Most of these increases exhibited statistically significant margins. The tested thermoplastic polymers include nylon-6, low-density polyethylene, low-density polyethylene/ethylene-vinyl acetate copolymer, and polyester. The percent composition of nanofiller was confirmed by thermogravimetric analysis and nanofiller distribution was analyzed using transmission electron microscopy.

I. INTRODUCTION

While polymer dielectrics store energy by distorting the electron distribution around the polymer chain, the amount of energy they can store is limited by the distortion's potential to cause breakdown of the bulk material. At some field strength, the electrons will have high enough energy to break from the polymer backbone. The localized accumulation of charge increases the likelihood of free electron formation in the presence of a high electric field. Although ideally a dielectric would experience a relatively uniform field, impurities and imperfections in the polymer matrix generally lower real-world dielectric strength, and electrode configuration also factors into field uniformity.

As soon as electrons are free within the dielectric, they are rapidly accelerated through the material by the applied field until they collide with another branch of the polymer. If the mean free path is long enough or the applied field is strong enough, the electrons can gain the kinetic energy necessary to free new electrons (or create UV photons) upon collision with the polymer. If each collision results in more than one electron being released on the average, then an exponentially increasing "electron cascade" will take place and will result in a disruptive breakdown of the dielectric.

Other discharges can damage the dielectric, but not lead to total failure. Types of detrimental discharge include corona formation, treeing, and tracking. These phenomena can result in slow degradation of the polymer, at times creating conductive pathways around or through the material. The conduction path may breach the bulk material or at least damage it enough so that the breakdown potential is lowered to the level of the applied voltage and a disruptive breakdown takes place.

The first test used in this study measures dielectric strength. This rating describes the peak applied field achieved under a specific electrode arrangement with a rapid potential ramp rate. It indicates the polymer's resistance to short-term breakdown at high field strengths.

The second test determines the endurance of the polymer under a lower applied field for an extended period. Under this moderate field strength a corona, which is an area of ionized gas emitting UV radiation, slowly breaks down the polymer at the surface. Ideally this method is used on samples of equal thickness under identical conditions (voltage, electrode configuration).

With respect to electrical breakdown, nano-films (nanofiller modified films) have shown improvements over their neat (unmodified) film equivalents. This has been demonstrated in the case of silica addition to epoxy [4] where corona resistance was increased over nine times with a silica addition of 4.7% by weight. Prior study into the addition of POSS to polypropylene showed a seven times increase in corona lifetime over the polypropylene with no filler [5]. In more recent work [6,7], breakdown strength of a control epoxy and a 5% by weight POSS loaded epoxy were compared. The epoxy with POSS showed a 33% increase in breakdown strength.

With reasoning taken from Nelson and Fothergill for their work on nanometer sized titanium dioxide in epoxy, nano-additives in thermoplastics may allow localized charge movement thereby minimizing bulk charge accumulation. This may keep localized internal fields low and aid in increasing dielectric breakdown strength [1].

Varlow and Li found that at low filler concentrations ($\leq 15\%$ by weight), the electrical properties of the polymer were prevalent, and the dielectric constant remains relatively unchanged with a varying applied field [2]. Higher filler concentrations may result in clumping, which would cause the nanofillers to act more like microfillers (micrometer-sized fillers). In some cases, microfillers have hurt electrical polymeric properties like the dielectric breakdown strength

[3]. This may be due to the relatively low surface-to-volume ratio of microfillers, since charge mobility is only aided at the filler-matrix interface [8].

In this study, variants of three polymers (polyethylene, nylon, and polyester) were tested for increases in their short-term dielectric strength as well as in their corona endurance with the addition of clay nanofillers.

Low density polyethylene (LDPE) is a mechanically tough, inexpensive polymer used heavily in industry. Numerous studies have sought the enhancement of its electrical, thermal, or mechanical properties through low-cost additives. Studies into nanofiller additives including titanium dioxide [1] and alumina [9] have shown significant increases in electrical breakdown strength with low ($\leq 10\%$ by weight) filler amounts.

A blend of LDPE grafted with maleic anhydride (LDPE-g-MA) is tested in this work for improved electrical properties with clay addition. The graft introduces polarization to the polymer backbone which allows for a more even dispersion of polar nanofillers. Previous work with grafting has improved dielectric strength and resilience to water treeing in neat samples without filler [10].

This study tests a linear low density polyethylene (LLDPE) copolymer with octene. LLDPE improves over regular LDPE in a number of mechanical properties, though it has a higher production cost.

A laminate of LDPE with ethylene vinyl acetate (EVA) was also investigated. In this sample, the EVA was of 0.75 mil thickness. This pair has previously been used to study local charge accumulation under DC voltage [11]. It is hypothesized [1] that this accumulation incites polymer dielectric breakdown. Improvement in the dielectric breakdown of this material would support the hypothesis that the nanofiller dissipates accumulated charge.

Nylon-6 is both tough and strong, while also holding potential as an example of green chemistry in commercial and industrial polymer research [12]. Samples of this and polyethylene terephthalate (PET) have also been included in the scope of this study. PET is a lightweight resin with variable rigidity. Its manufacture accounts for a large part of the overall polymer industry, only behind that of polyethylene and polypropylene.

The use of inexpensive nanofillers to strengthen thermoplastics against electrical failure extends their usefulness in high voltage applications, but polymer interactions are very difficult to generalize. Due to potential performance benefits of these modifications, this study has set out to survey a range of polymers for improvement with the use nanoclay filler.

II. EXPERIMENTAL METHOD

All thermoplastics were received as manufactured in film form with thicknesses ranging from 20 to 104 μm . Clay nanoadditives were added during manufacture up to 15% by weight. The weight percent and distribution of each polymer sample were investigated using thermogravimetric analysis and transmission electron spectroscopy.

The short-term dielectric withstand tests were performed with ASTM standard D 149 electrodes [13]. Each rod electrode was 6 mm in diameter with a 0.8 mm radius at the tip edge. The sample was placed between two identical, aligned rods. A special fixture was designed to hold the samples, inhibit surface flashover (without insulating gas or liquid immersion), and enable bulk breakdown. Sixty Hz ac voltage was applied from a Biddle 582040KV-3 KVA power supply at an approximate rate of increase of 0.96 kV/s. A minimum of 14 samples were tested for each polymer type. Voltage readings were taken with a Northstar VD-60 probe connected to a Tektronix TDS 3054B oscilloscope.

The corona endurance tests were undertaken following the setup of the ASTM standard D 2275 test [14]. The upper electrode was 6 mm in diameter with a 0.8 mm radius at the tip edge, and the lower electrode was 25 mm in diameter with a 3 mm radius at the tip edge. The sample was cut so that it would cover most of the lower electrode's surface, and was placed between the two electrodes. The voltage was quickly increased to 2.25 kV of 60 Hz ac and then maintained at the test voltage. The power supply included a Trek 662 & 663A high voltage amplifier utilizing a Wavetek 275 function generator source. The same Northstar VD-60 probe and Tektronix TDS 3054B oscilloscope were used for measurement. Custom circuitry was employed to record the timing of individual breakdown events.

The tested filler, montmorillonite, is a natural clay which consists of crystallized platelets of $(\text{Na,Ca})(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$. It is highly hygroscopic, and expands to several times its dry volume with the addition of water. In this study, exfoliated platelets of the clay are used, and manufacture was carried out so as to distribute the layers evenly through the film. Single platelets are on the order of 1 nm thick, with a range of diameters, from 50 to hundreds of nanometers. The surface of the montmorillonite layers is modified with surfactants, typically octadecyl ammonium, for increased compatibility with synthetic polymers. The particular formulations for chemical modifications of the montmorillonite, as well as processing details, are proprietary.

III. RESULTS AND DISCUSSION

In short term tests, all nanocomposite samples showed increased average dielectric strength over their respective neat counterparts. The averages and standard deviations for all test data obtained in this study can be found in Table 1.

The LLDPE film achieved a 19% increase with a 2.39 wt% addition of filler. Transmission electron micrographs of film cross-sections at low and high magnification (Figures 1A and 1B) show moderately good dispersion of the clay layers, with some individual layers present but mostly aggregates of 2-40 layers. The LDPE/EVA films were also tested, and the experimental film with 1.30 wt% filler added showed a 5% increase in dielectric strength. The LDPE-g-MA set underwent a 28% increase in dielectric strength with 5.71 wt% of nano-sized clay filler added. These results indicate a general benefit in dielectric breakdown strength with addition of clay nanofiller to polymers, however processing and the

TABLE I
RESULTS OF DIELECTRIC STRENGTH AND CORONA ENDURANCE TESTS

Sample (weight % clay)	Dielectric Strength Tests		Corona Endurance Tests	
	Average (kV/mm)	σ (kV/mm)	Median Time of Breakdown (h)	Sample Height (μm)
LLDPE (0%)	207	40.1	17.5	44
LLDPE (2.39%)	247	32.2	87.3	68
LDPE/EVA (0%)	133	24.9	19.9	60
LDPE/EVA (1.30%)	140	22.8	24.1	52
LDPE-g-MA (0%)	202	37.0	24.1	49
LDPE-g-MA (5.71%)	257	28.5	50.6	45
Nylon-6 (0%)	66	8.7	7.5	55
Nylon-6 (2.84%)	75	3.4	60.8	70
Nylon-6 (2.96%) ¹	99	6.8	-	26
Polyester (0%)	139	18.5	22.2	80
Polyester (12.87%)	217	34.9	50.4	57
Polyester (14.53%)	156	24.1	51.4	67

¹ Sample was too thin for comparable corona endurance testing

subsequent morphology obtained is a key component in maintaining such benefits, as the following results demonstrate.

Nylon-6 2.84 wt% (Figures 1C and 1D) and Nylon-6 2.96 wt% (Figures 1E and 1F) increased by 13% and 49% respectively over the breakdown strength of the pure Nylon-6 film. TEM images of the 2.84% sample showed micron-sized aggregates, which may lead to a lower than expected breakdown strength. Aggregation due to excessive nanoparticle loading is not expected to be the reason for the poor performance of the 2.84% sample, as each sample has a similar weight percent loading.

Polyester with 12.87 wt% nanofiller showed a 56% increase over the neat polyester film, however with further addition of nanofiller this trend did not continue. TEM images of polyester nanocomposites with 12.87% loading are shown in Figures 1G and 1H and 14.53% loading in Figures 1I and 1J. The low and high magnification micrographs for each sample show that they both exhibit uniform distribution of nano-sized clay aggregates, with the aggregates containing approximately 2-20 clay layers each. Only in the nanocomposite with higher loading, however, were larger micron-sized aggregates visible (Fig. 1I, inset). These micron-sized aggregates are likely to contribute significantly to lower than expected breakdown strength measured for the 14.53% polyester nanocomposite.

Other possible reasons for decreased breakdown strength in addition to nanoparticle aggregation include losses due to leakage current that result in local damage or heating, increasing the odds of an electron cascade taking place at lower electrical field strengths. Varlow and Li noted a certain

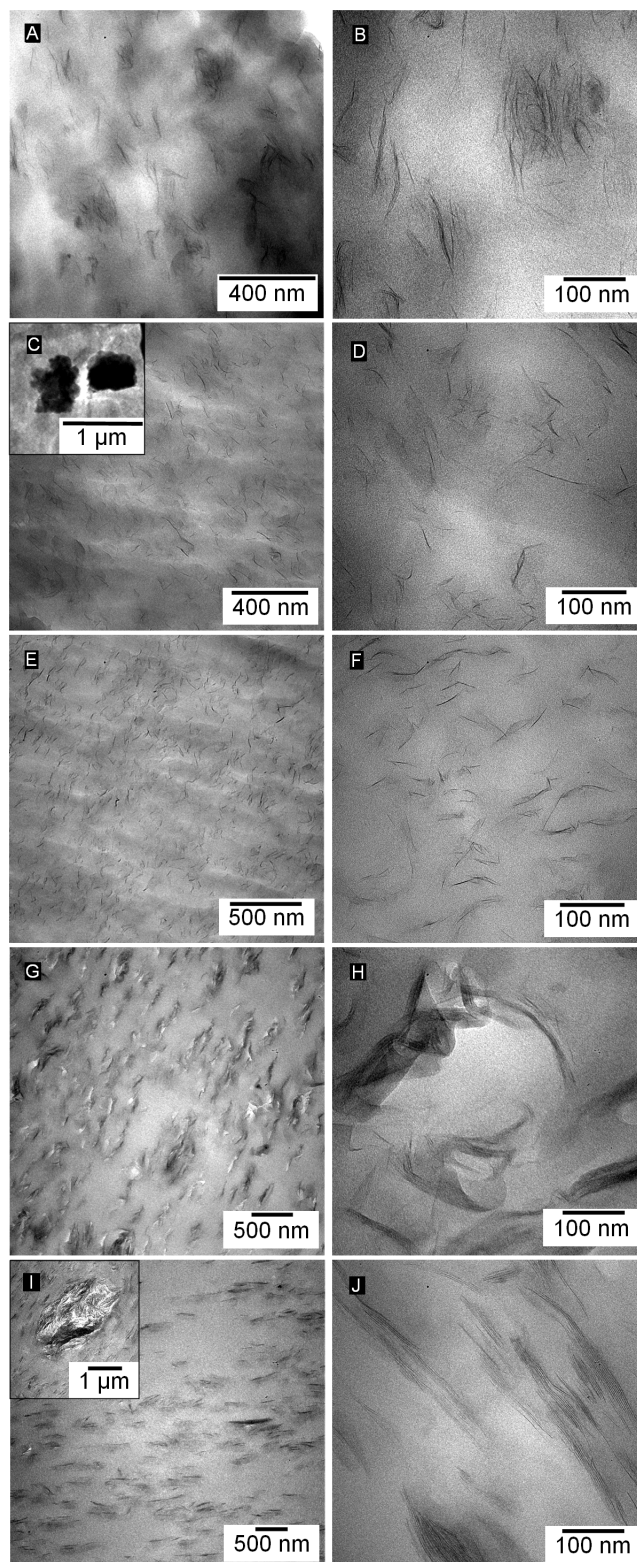


Fig. 1. TEM images of nanofiller modified thermoplastics. A and B show LLDPE (2.39%), C and D show Nylon-6 (2.84%), E and F show Nylon-6 (2.96%), G and H show Polyester (12.87%), and I and J show Polyester (14.53%).

weight percent loading at which the dielectric character would be substantially determined by the bulk qualities of the filler material [1]. At high filler percents, the electric field density in the low dielectric constant polymers may be increased as well, since the field would preferentially locate in the lower permittivity polymer.

Using the Student's t-test ($\alpha=0.05$), all film samples were found to have statistically significant increases in dielectric strength after filler addition with the exception of the LDPE/EVA films.

Long term tests again showed improvement with filler addition, with one exception. The nylon-6 (2.96%) sample showed a drastic drop in lifetime. This sample was prepared as an extremely thin film, which likely biased these results beyond easy interpretation for corona endurance. The methodology used for the other samples calls for an applied voltage which is almost at the short-term breakdown strength of this film (~2 kV).

LDPE with 2.39% loading showed nearly a fivefold increase in median time to breakdown, nylon-6 with 2.84% loading showed an eightfold increase, and both polyester (12.87% and 14.53%) samples showed more than a twofold increase with respect to the neat polymers.

IV. SUMMARY AND CONCLUSIONS

Thermoplastic samples with nano-additives showed statistically improved dielectric breakdown strength when compared to neat samples, but the contributions to these gains were varied as a function of percent nanoclay added. This implies a complex set of both manufacturing and experimental variables. A similar gain in corona endurance was noted in most samples which were modified with nanoclay. Exceptions in both cases can be attributed to micron-scale morphological defects cause by over loading of nanoparticles or processing defects.

The decrease in breakdown strength of nanocomposite at high filler concentration may suggest an upper limit to electrical augmentation. Varlow and Li [1] noted in their study on a PZT (Lead Zirconate Titanate) polyester composite films that filler contents <15 wt% would have electrical properties most like that of the polymer, but high concentrations of filler could lead to high losses and low dielectric strength. A second concern that the high-k filler will displace electrical field density into the low-k polymer could mean that samples with high filler concentrations are effectively equivalent to thinner samples.

Low standard deviation in most fast-rate tests could hint at means of controlling the dielectric breakdown strength of these and other polymers. While the increases found in this study were often nonlinear especially at higher concentrations, studies which probe more deeply into the gains achieved with varying filler levels in individual films could search for optimal levels of clay nanofiller specific to each material. In further research, care must be taken to manufacture materials with minimized variance, so that experimental variables can be more clearly elucidated.

ACKNOWLEDGMENTS

We would like to thank Marlene Houtz, Julie Kubicki, and Gary Webb for their assistance in performing these experiments; as well as Triton Systems Inc., Honeywell, Ampacet, and Dow Chemical Company for providing the neat and modified polymer samples.

REFERENCES

- [1] J. K. Nelson and J. C. Fothergill, "Internal Charge Behavior of Nanocomposites," *Nanotechnology*, Vol. 15, 2004, pp. 586-595.
- [2] B. R. Varlow and K. Li, "Non-linear AC Properties of a Ceramic/Resin Composite," *Proceedings of the 6th International Conference on Properties and Applications of Dielectric Materials*, Xi'an, China, 2000, pp. 89-92.
- [3] J.K. Nelson, "The Promise of Dielectric Nanocomposites," *Conference Record of the 2006 IEEE International Symposium on Electrical Insulation*, Toronto, Canada, 2006, pp. 452-457.
- [4] P.O. Henk, T.W. Kortsen and T. Kvarts, "Increasing the Electrical Discharge Endurance of Acid Anhydride Cured DGEBA Epoxy Resin By Dispersion of Nanoparticle Silica," *High Perform. Polym.*, Vol. 11, 1999, pp. 281-296.
- [5] J. Horwath and D. Schweickart, "Inorganic Fillers for Corona Endurance Enhancement of Selected Polymers", in *Conference Record of the Twenty-Fifth International Power Modulator Symposium*, Hollywood CA, 2002, pp. 644-647.
- [6] J. Horwath, D. Schweickart, G. Garcia, D. Klosterman and M. Galaska, "Improved performance of polyhedral oligomeric silsesquioxane epoxies", 2005 Annual Report on Conference on Electrical Insulation and Dielectric Phenomena, IEEE Dielectrics and Electrical Insulation Society, October 2005, pp. 155-157.
- [7] J. Horwath, et al., "Improved Electrical Properties of Epoxy Resin with Nanometer-Sized Inorganic Fillers", in *Conference Record of the Twenty-Seventh International Power Modulator Symposium*, Washington DC, 2006, pp. 189-191.
- [8] M. Roy, et al., "Polymer Nanocomposite Dielectrics – The Role of the Interface", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 12, 2005, pp. 629-643.
- [9] Y. Cao, P. Irwin and K. Younsi, "The Future of Nanodielectrics in the Electrical Power Industry," *Trans. DEI*, Vol. 11, No. 5, Oct. 2004, pp. 797-807.
- [10] K. Suh, C.R. Lee, Y. Zhu, "Electrical Properties of Chemically Modified Polyethylenes", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 4, 1997, pp. 681-687.
- [11] T. Tanaka, O. Kisanuki, M. Sakata, and M. Uchiumi, "Characteristics of Space Charge Formed in a Laminated LDPE/EVA Dielectric under DC Stress", in *Converence Record of the 1996 IEEE International Symposium on Electrical Insulation*, Quebec, Canada, 1996, pp. 184-187.
- [12] M. Braun, A.B. Levy, S. Sifniades, "Recycling Nylon-6 Carpet to Caprolactam," *Polymer-Plastics Technology and Engineering*, Vol. 38, No. 3, 1999, pp. 471-484.
- [13] *ASTM D 149 Standard Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies*, in Annual Book of ASTM Standards, American Society for Testing and Materials: Conshohocken, PA., 1992.
- [14] *ASTM D 2275 Standard Test Method for Voltage Endurance of Solid Electrical Insulating Materials Subjected to Partial Discharges (Corona) on the Surface*, in Annual Book of ASTM Standards, American Society for Testing and Materials: Conshohocken, PA., 1992.